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Modelling point and diffuse heavy metal emissions and loads in the Elbe basin

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Abstract:

The reduction of pollutant loads in rivers requires a good comprehension of the contribution of all major (point and diffuse) sources in each sub-basin. Due to the sudden change of a centrally planned economy to a free-market economy in 1989, the River Elbe is one of the fastest changing transboundary river basins in Central Europe. The quantification of fluxes of heavy metals in the Elbe basin requires information on the spatial and temporal characteristics of emissions and on physical boundary conditions of the entire river basin. In this paper, a GIS-based model METALPOL will be presented, that describes the load of five heavy metals (Cd, Cu, Hg, Pb, Zn) in the Elbe basin over the period 1985–1999 as a function of (1) emissions from point and diffuse sources, (2) runoff, (3) soil types, (4) land use and (5) hydrogeology. The results from the model were validated with the measured heavy metal loads and showed reasonable agreement. Between 64% (for Hg) and 84% (for Pb) of the total heavy metal emissions in the Elbe basin is supplied by inputs from diffuse sources. The diffuse hydrological pathways with the highest share are erosion and urban areas. In most cases the measured heavy metal load is lower than the sum of the heavy metal emissions. Retention processes (e.g. sedimentation) largely explain this behaviour and are found to be dependent on the specific runoff of a catchment. About 81–97% of variance for the different heavy metals can be explained by the dependency on specific runoff. The uncertainty analysis presented in this paper has also illustrated that the reliability of the model simulations is directly affected by the quality of the input data (especially point source and urban emissions) and the distribution of the input data like rainfall data, emission data, soil data and land cover data. Finally, scenario analysis indicated that the current proposed measures are not stringent enough to achieve large reductions in heavy metal loads in the Elbe basin. Copyright © 2003 John Wiley & Sons, Ltd.

KEY WORDS Elbe; heavy metals; point and diffuse sources; heavy metal emissions; heavy metal load; source apportionment; river system; retention

INTRODUCTION

The concentration of heavy metals in large rivers and coastal waters is influenced by emissions from point and diffuse sources. Although concentrations have declined over the years, there is still a threat to the provision of freshwater of an acceptable quality. Several management strategies have succeeded in reducing pollutant fluxes, especially heavy metals, in large river basins like the Rhine and Elbe. These management strategies first focused on the reduction of point source emissions (IKSE, 1995), but still some water quality criteria are not met. Therefore, additional measures are required based on an insight into the spatial distribution of emissions within a river basin. Many studies have looked at local problems of heavy metal contamination, but only few have studied heavy metal fluxes at the river basin scale (Behrendt, 1993, Vink *et al*., 1999a,b; Mohaupt *et al*., 2000). The aim of this study was to develop, analyse and apply a large-scale water quality model, designed to:

- Analyse pathways or apportion sources of heavy metals through a river basin; identifying all important sources and pathways of heavy metals in a river basin.

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- Integrate and translate different types of data (e.g. maps, time series, tables) of different scales to relevant parameters at a river basin scale.
- Analyse how transport and retention processes influence the heavy metal fluxes from their multiple sources throughout a river basin.
- Predict and evaluate possible effects of source reduction of heavy metals within river basins on heavy metal loads throughout the river basin.

In order to assess long-term and large-scale historic, current and future heavy metal fluxes in the Elbe basin, the heavy metal fluxes were evaluated with respect to large-scale river basin characteristics. The analysis is based on emission estimates from point and diffuse sources, hydrology, lithology and water quality data and covers the period 1985–1999. The sensitivity of the simulated discharge and heavy metal loads (by the model METALPOL) to different model parameters was investigated with a simple sensitivity analysis. Further, the effects of emission reduction measures on the heavy metal emissions in the Elbe river basin up to the year 2020 were investigated.

STUDY AREA: ELBE BASIN

The Elbe drainage area covers an area of 148 268 km^2. It is divided over four countries: Germany (96 932 km^2), Czech Republic (50 176 km^2), Poland (240 km^2) and Austria (920 km^2) (IKSE, 1995). Figure 1 shows the location of the Elbe river basin. Table I describes some general characteristics of the different

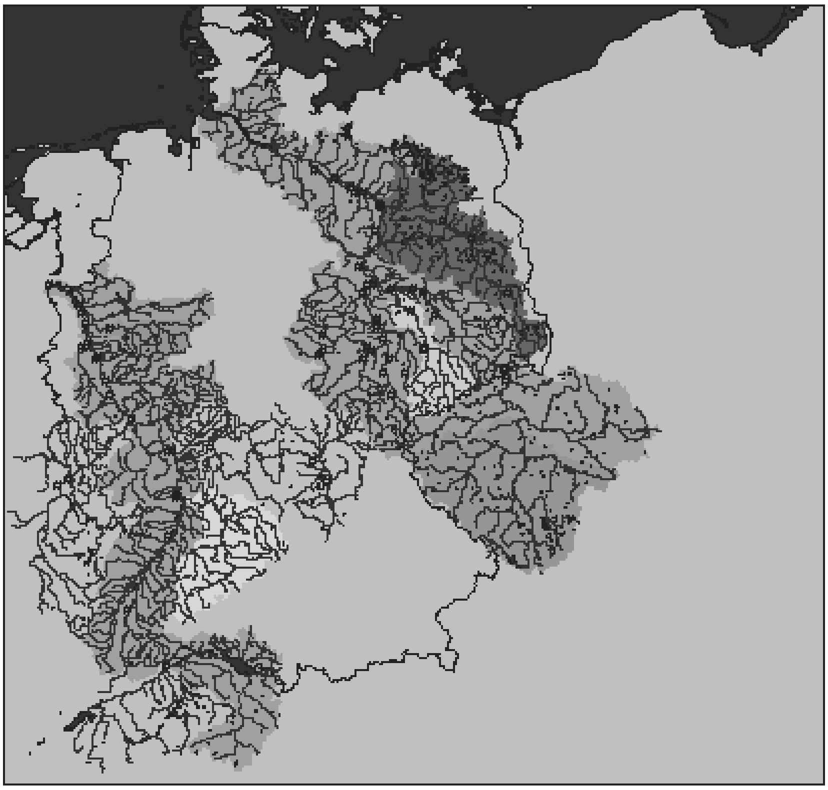


Figure 1. Geographical overview of the Elbe basin, main tributaries and monitoring stations

Table I. General characteristics of the rivers Elbe, Rhine, Scheldt, Weser and Meuse

River; station	River length (km)	Catchment (km^2)	Average discharge ($m^3\ s^{-1}$)	Population (inhabitants)
Elbe; Neu Darchau	536·4	131 950	720	23 million
Rhine; Lobith	862·8	159 127	2170	45 million
Scheldt; Schaar	355	21 000	129·4	10 million
Weser; Hemelingen	440	38 415	360	9 million
Meuse; Eijsden	860	31 000	220	9 million

catchments, which discharge to the North Sea. In European terms the Rhine and Elbe basins are medium to large-sized river basins.

In the Elbe drainage area 25·2 million people are living, of which 19·1 million are in Germany and 6·1 million in the Czech Republic. The biggest urbanized areas in the Elbe catchment are Berlin, Hamburg, Prague, Leipzig, Dresden, Halle, Chemnitz and Magdeburg. About 55% of the total area in the Elbe catchment is agricultural land and 29% is covered with forests. The Elbe River can be characterized as a 'rain–snow' type. It has its origin in Spindleruv Myln in the Czech Republic at an altitude of 1384 m and has a length of 1091 km. High discharge periods occur in the winter and spring period, after periods of rainfall. The mean discharge of the Elbe River at gauging station Neu-Darchau (catchment outlet) is 720 $m^3\ s^{-1}$. The Elbe drainage area represents a good example of a river system that has experienced a rapid change in economic conditions (central to the market economy) with a corresponding change in heavy metal fluxes in the river basin.

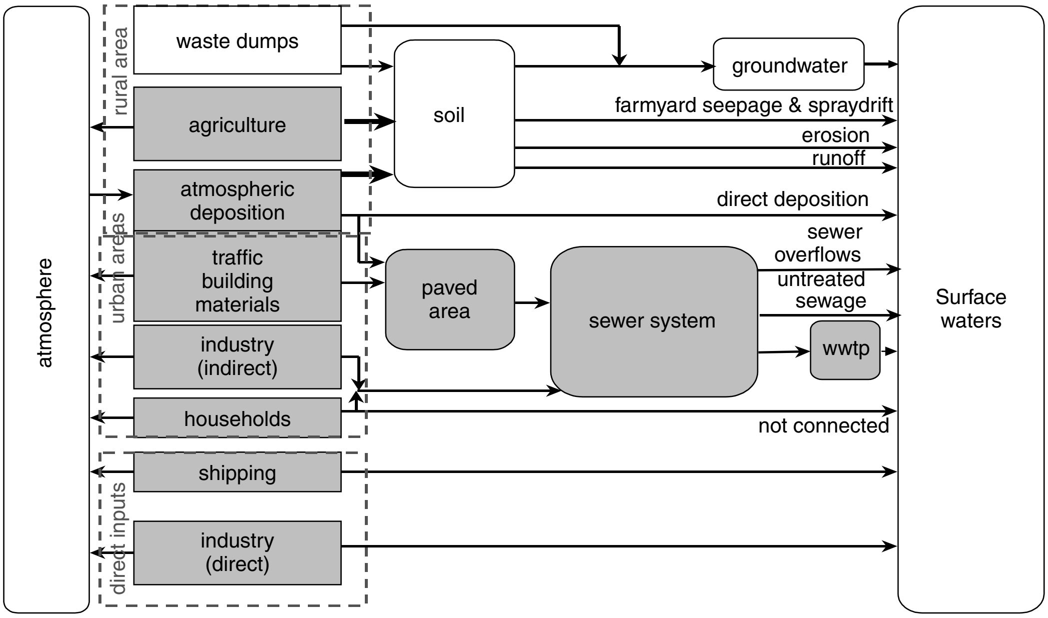
METHODOLOGY AND MATERIALS

The amount of point and diffuse sources in large river basins is normally too numerous to make inventories of all individual sources and pathways for each location in a river basin. Therefore, a generally accepted alternative is to use emission factors and regional statistics to estimate emissions for a more regional level (Vink *et al*., 1999a). In Figure 2 an overview is given of different pathways of heavy metals in large river basins as considered in this study.

The model METALPOL uses different types of data (see Table II):

- emission data for model input;
- physical data on the characteristics of the river basin, needed to describe the behaviour of heavy metals;
- measurements on rainfall and temperature as model input and water quality data for the calibration and validation of the model.

A GIS database on heavy metal emissions from non-point and point sources to the soil surface and surface water was constructed, containing data on livestock, population, type of wastewater treatment, connection rate, traffic, large industrial emissions, fertilizer usage, building materials, atmospheric deposition, (sewage) sludge and shipping (Vink *et al*., 1999a). Point sources emissions estimates cover inputs from industries and wastewater treatment plants during the period 1985–1999. Heavy metal emissions are estimated using emission factors for heavy metals (e.g. heavy metal excretion per animal, heavy metal content of sewage sludge, heavy metal excretion per human and heavy metal release per car) and applied to administrative units. These emission factors were gathered from various surveys (Vink *et al*., 1999a). The study produced a series of maps covering the period from 1985 to 1999, with yearly estimates of heavy metal inputs to soil and water compartments. These yearly estimates are then used as input into METALPOL. Data on the physical characteristics of the catchment are needed to describe the behaviour of the transport of heavy metals. METALPOL requires, besides heavy metal emissions, a number of geographical data sets which



Point Sources are defined as: Industry and wastewater treatment plants (WWTP)
Diffuse sources are: Emissions from urban areas :(1) inputs from paved urban areas connected to separate sewer systems (SSS), (2) inputs from paved urban areas by combined sewer overflows (CSS), (3) inputs from households and paved urban areas connected to sewers without WWTP's (Sewer) and (4) inputs from households and paved urban areas which are not connected to sewer systems (No sewer) ; direct atmospheric deposition; erosion; groundwater; fast runoff; shipping and agriculture.

Figure 2. Pathways of heavy metals in river basins

cover topography, drainage network, land use, hydrogeology and soil types. Measurements are needed for both model input and model calibration and validation. Rainfall and temperature data were gathered for about 30 stations in the Elbe basin. Heavy metal loads are derived from water quality data measured at about 25 monitoring stations in the Elbe basin. The data from 1985–1990 was used to calibrate the model and the monitoring data from 1991–1999 was used to validate the model.

The model METALPOL describes a river basin as a series of related storages translating gross heavy metal emissions, which are controlled by the water balance of a certain catchment, into river loads. METALPOL is GIS-based (PC-Raster, 1996) and contains a set of utilities for hydrological and geomorphological modelling. Hence, each gridcell (of 1 km^2) contains soil and groundwater storage compartments. The air compartment is used as a boundary condition, which means that atmospheric deposition is supplied as input into METALPOL. Heavy metal flows between storage compartments are controlled by chemical and physical characteristics of soil, land use, climate and hydrogeology.

The method used to describe the transport of heavy metals from their sources to river loads in METALPOL is given in Equation (1):

$$L_{i,T}^{M} = [E_{\text{industry}} + E_{\text{wwtp}} + E_{\text{urban}} + E_{\text{gw}} + E_{\text{fast}} + E_{\text{erosion}} + E_{\text{atm}} - E_{\text{retention}}] \tag{1}$$

$L_{i,T}^{M}$ = total load of a given substance M at monitoring station i over a certain time period T [t a^{-1}]
E_{industry} = annual average industrial emissions to the surface water upstream of location i [t a^{-1}]
E_{wwtp} = annual average emissions from wastewater treatment plants to the surface water upstream of location i [t a^{-1}]

Table II. Data needed for the analysis of heavy metal fluxes in the Elbe basin

Type	Data	Resolution	Reference
Emission	Livestock, population numbers, type of wastewater treatment, connection rate, traffic, fertilizer usage, building materials, atmospheric deposition, (sewage) sludge and shipping	Administrative units	Vink (2002)
	Large industrial emissions	Exact location	IKSE (1992, 1995, 2000)
Physical characteristics	Land use	1×1 km^2	IKSR (1999)
	Hydrogeology	1×1 km^2	IAH (various years)
	Soil	1×1 km^2	Bundesanstalt für Geowissenschaften und Rohstoffe (German) and Research Institute for Soil and Water Conservation Prague (Czech)
	Elevation	1×1 km^2	United States Geological Survey (USGS)
Measurements	Rainfall, temperature, discharge, heavy metal loads		Bundesanstalt fur Gewasserkunde; Federal States and Arge-Elbe

E_{urban} = annual average emissions from urban areas to the surface water upstream of location i [t a^{-1}]
E_{gw} = annual average groundwater emissions to the surface water upstream of location i [t a^{-1}]
E_{fast} = annual average emissions from fast runoff (surface runoff and interflow) to the surface water upstream of location i [t a^{-1}]
E_{erosion} = annual average emissions from erosion to the surface water upstream of location i [t a^{-1}]
E_{atm} = annual average emissions from direct atmospheric deposition to the surface water upstream of location i [t a^{-1}]
$E_{\text{retention}}$ = annual average retention of material in surface waters upstream of location i [t a^{-1}]

Behrendt and Opitz (1999) analysed the retention of nutrients in river systems by evaluating the relation between the sum of all point and diffuse sources of nutrient emissions, which represents the inputs into a catchment, and the measured load (immission or output) of nutrients. They found that the loss or retention of nutrients (N and P) in a river system was strongly related to the specific runoff (q) as illustrated in Equation (2). When the specific runoff of a catchment is high the retention tends to be low, and when the specific runoff is low the retention tends to be high:

$$E_{\text{retention}} = \frac{L_{i,T}^{M}}{E_{i,T}^{M}} = \frac{1}{1 + a \cdot q_{i,T}^{b}} \tag{2}$$

$E_{i,T}^{M}$ = total emissions of a given substance M at monitoring station i over a certain time period T [t a^{-1}]
$q_{i,T}$ = specific runoff of catchment i over a certain time period T [l km^{-2} s^{-1}]
a, b = constants estimated by non-linear regression [–]

Behrendt and Opitz (1999) estimated the values at $a = 26{\cdot}6$ and $b = -1{\cdot}71$ for P, using 89 different river basins in Europe. In METALPOL, this formulation was used as a basis for deriving different retention functions for the transport of some heavy metals in the River Elbe.

PATHWAYS IN METALPOL

Surface water balance

The main pathways in the model METALPOL, describing the transport of heavy metals, are fast runoff (interflow and surface runoff), slow runoff (groundwater), erosion and the direct heavy metal inputs from urban areas, industry and wastewater treatment plants. Pollution from diffuse (indirect) sources is mainly related to rainfall and excess water available for runoff. The total runoff was calculated with a water balance model that is based on Rhineflow (Kwadijk, 1993) and simulates fast and slow runoff for each 1 km^2. METALPOL uses meteorological data (temperature and rainfall), soil types, land use and elevation. Combined with the necessary input, evapotranspiration and runoff using the Thornthwaite–Mather method are calculated. The calculated water surplus per year is divided into a rapid runoff and a slow runoff component using separation coefficients and recession coefficients. The separation coefficient is calculated as a function of soil characteristics and slope (de Wit, 1999). The recession coefficient is calculated on the basis of hydrogeological properties. The heavy metal input by fast runoff is calculated as the product of the amount of fast runoff and the estimated runoff concentration. The heavy metal concentration in the fast runoff is derived from the heavy metal balance in the topsoil and several soil properties (Romkens, 1998).

Leaching to groundwater

The heavy metal content of the soil changes temporally due to changes in the supply of heavy metals from e.g. atmospheric deposition and by the application of manure and fertilizer. Strong leaching of pollutants to the groundwater will only occur under acid conditions (Stigliani, 1988). Heavy metals are strongly bound to the solid phase of the soils, and only a small fraction is available for leaching. The transport of heavy metals along the groundwater pathway is determined by calculating a measured regional specific heavy metal concentration in the groundwater (Fauth *et al*., 1985). This is multiplied by the groundwater volume as calculated by the water balance model.

Erosion

Another important pathway in the transport of heavy metals is erosion. Behrendt *et al*. (1999) developed a method to derive the nutrient emissions via erosion, which was adapted for heavy metals. The heavy metal inputs by erosion are calculated as the product of the heavy metal content of soil, the specific enrichment ratio model, the sediment delivery ratio, the weighting factor and the soil loss as shown in Figure 3. The soil loss in the river basins was calculated according to the modified USLE (universal soil loss equation). For the estimation of the sediment delivery ratio (SDR) a new GIS-supported method has been proposed by Behrendt *et al*. (1999) that involves a separation of areas which contribute to soil loss into the river systems. Through regression analysis, the mean slope of a basin and the portion of arable land were identified as parameters that explain most of the variance in the SDR. This relationship was validated using long-term daily records of measurements of suspended solids for 23 river basins in Bavaria and Baden-Württemberg. To adapt the erosion estimates for differences in hydrological conditions between the time periods a weighting factor, which considers the number of days with high flow, was introduced for this study according to Rogler and Schwerdtmann (1981). The heavy metal content of the agricultural soils for the different regions were derived from LABO (1998).

Heavy metal concentrations in suspended material tend to be higher than in the upper soil because of the enrichment of smaller particles during the process of erosion and the preference of smaller particles transported

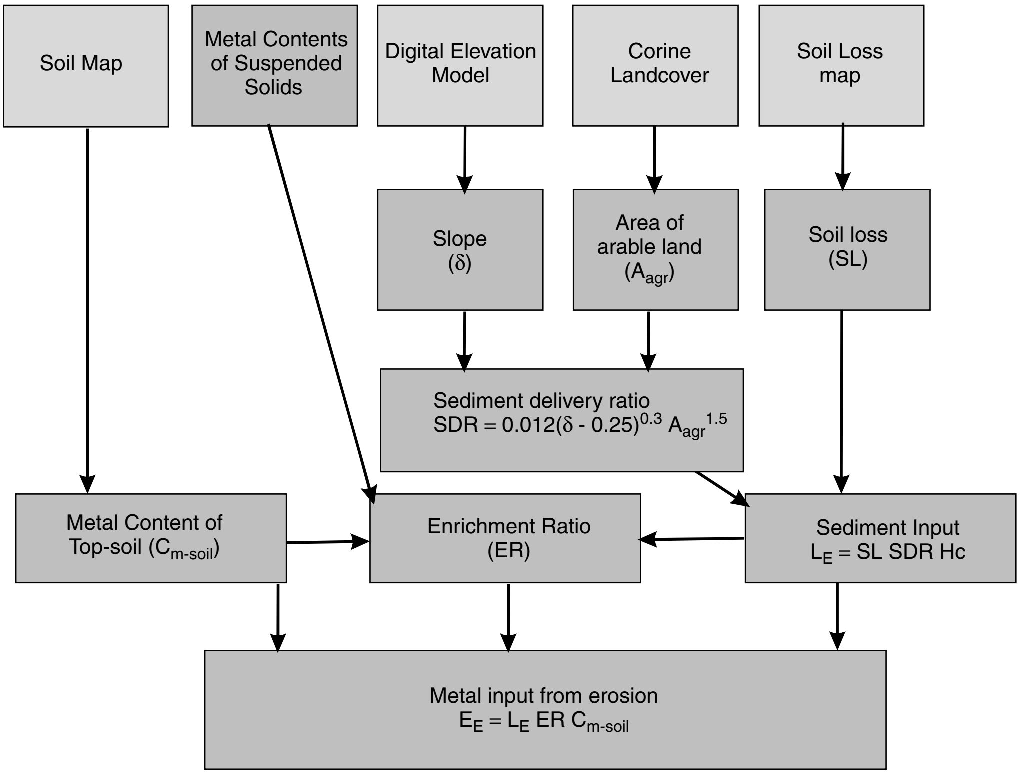


Figure 3. Scheme for the estimation of heavy metal inputs by erosion (adapted from Behrendt *et al.*, 1999)

from the soil to the river. Enrichment is defined as:

$$\mathrm{ER} = C_{\mathrm{M,SPM}}/C_{\mathrm{M-soil}} \tag{3}$$

where $C_{\mathrm{M,SPM}}$ is the heavy metal concentration in the suspended matter (mg kg^{-1}).

Behrendt *et al.* (1999) found that the enrichment ratio for P is reverse proportional to the square root of the specific sediment input. For each heavy metal considered in this study, data was gathered on average heavy metal concentrations of suspended particulate matter from several smaller rivers with negligible influence of point sources (Donau, Rhine and rivers in Mecklenburg Vorpommern). Average heavy metal concentrations of the topsoil in these small catchments were calculated. From these data, enrichment ratios were calculated [see Equation (3)] for each of the monitoring stations where data on heavy metal contents of suspended particulate matter was available. Assuming that heavy metals behave the same as P bound to suspended particulate matter, the enrichment ratio for each of the heavy metals was plotted versus the specific sediment yield of the catchment (Figure 4) and a log–log relation was determined.

RESULTS

By using the two different characteristic periods for calibration and validation, the model can be tested on its performance. The model was calibrated on the period 1985–1990, which is characterized by relatively wet conditions and validated for the period 1991–1999, which also includes a number of relatively dry years. The model was calibrated by means of least squares fitting and by maximizing the Nash–Sutcliffe efficiency criterion E and the model efficiency criterion ME used as objective functions in the optimization (Table III).

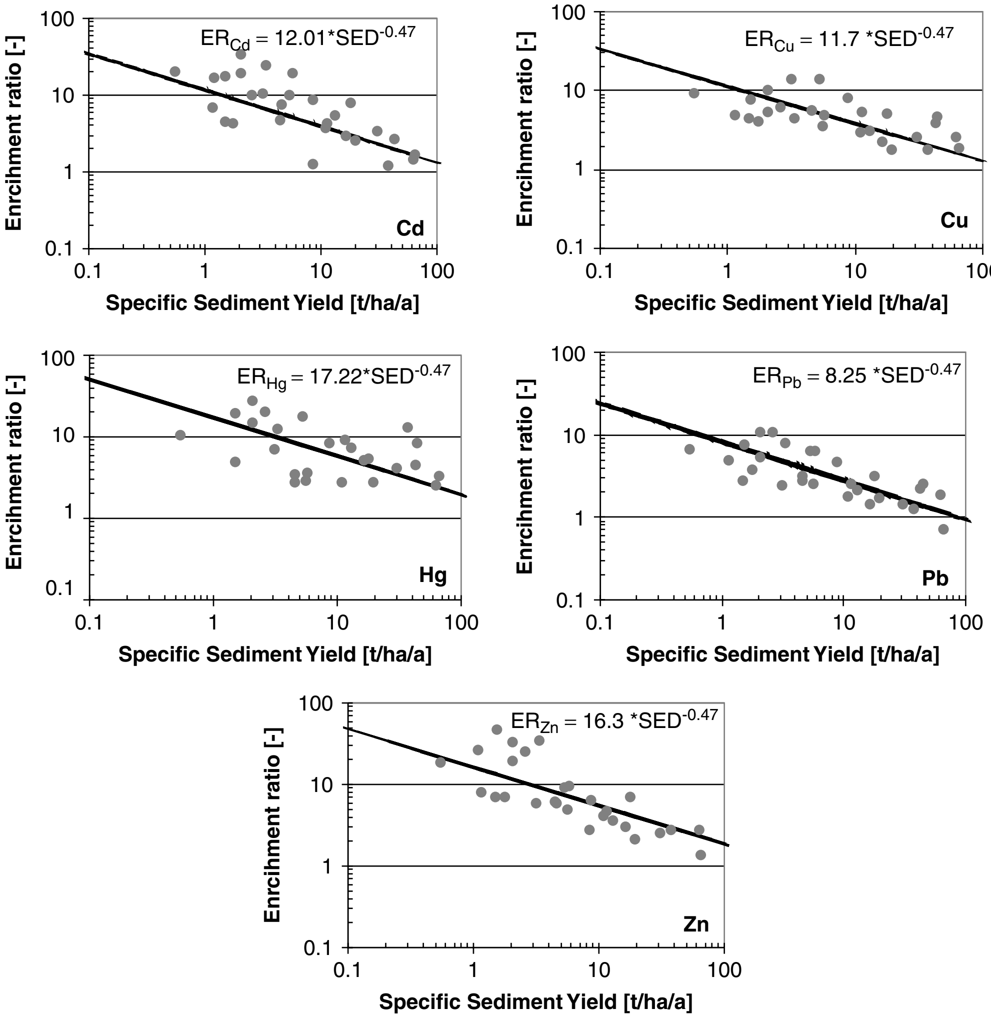


Figure 4. Relationship between enrichment ratio of heavy metals [as calculated according to Equation (3)] and the specific sediment yield

Another criterion used for the model evaluation is the relative volume error between simulated discharges and measured discharges and between simulated heavy metal loads and measured heavy metal loads.

Heavy metal emissions

Since 1990, heavy metal emissions decreased markedly. The economic changes instigated a decline in emissions (to water and atmosphere), resulting in a decrease in fertilizer usage and an increase in unleaded petrol sales. Heavy metal emissions in the Elbe basin over the period 1985–1999 are shown in Figure 5. The decrease of heavy metal emissions from industry is evident from Figure 5. This counts for both the relative contribution of the industrial sources to the total heavy metal emissions as well as the absolute contribution of industrial heavy metal emissions to the total heavy metal emissions. Both the absolute and relative amount of heavy metal emissions caused by point sources (the sum of industries and wastewater treatment plants) in the Elbe basin have rapidly decreased (see Figure 5). The contribution of point sources to the total emissions over the period 1995–1999 ranges from 16% (Pb) to 36% (Hg). Whereas the absolute contribution of diffuse sources is also decreasing, the relative contribution of diffuse sources to the total heavy metal emissions is

Table III. Model performance indicators

Discharge	Heavy metal load
$\mathrm{E} = 1 - \frac{R^2}{\mathrm{Var}(Q_{\mathrm{obs}})} = 1 - \frac{\sum (Q_{\mathrm{obs}} - Q_{\mathrm{mod}})^2}{\sum (Q_{\mathrm{obs}} - \overline{Q})^2}$	$\mathrm{ME} = 1 - \frac{R^2}{\mathrm{Var}(L^M_{\mathrm{obs}})} = 1 - \frac{\sum (L^M_{\mathrm{obs}} - L^M_{\mathrm{sim}})^2}{\sum (L^M_{\mathrm{obs}} - \overline{L^M_{\mathrm{obs}}})^2}$
E Nash efficiency [–]	ME model efficiency [–]
Q_{obs} yearly average observed discharge [$\mathrm{m^3\ s^{-1}}$]	L^M_{obs} observed heavy metal load [$\mathrm{t\ a^{-1}}$]
Q_{mod} yearly average simulated discharge [$\mathrm{m^3\ s^{-1}}$],	L^M_{sim} simulated heavy metal load [$\mathrm{t\ a^{-1}}$]
R sum of squares of the residuals [–]	R sum of squares of the residuals [–]
$\mathrm{Var}(Q_{\mathrm{obs}})$ variance of the yearly average observed discharge [–]	$\mathrm{Var}(L^M_{\mathrm{obs}})$ variance of the observed values [–]
$\overline{Q}$ long-term average yearly observed discharge [$\mathrm{m^3\ s^{-1}}$]	$\overline{L^M_{\mathrm{obs}}}$ long-term average observed heavy metal load [$\mathrm{t\ a^{-1}}$]
$\mathrm{Error} = \left(n^{-1}\left(\sum_{i=1}^{n}(Q_{\mathrm{obs}} - Q_{\mathrm{mod}})^2\right)^{0\cdot5}\right)$	$\mathrm{L\_Error} = \left(n^{-1}\left(\sum_{i=1}^{n}(L^M_{\mathrm{obs}} - L^M_{\mathrm{sim}})^2\right)^{0\cdot5}\right)$

increasing in the Elbe basin. The relative contribution of diffuse source emissions to the total heavy metal emissions ranges from 64% (Hg) to 84% (Pb). Figure 5 shows that diffuse sources are mainly dominated by inputs from urban areas, erosion and groundwater. Further, direct heavy metal emissions from urban areas (i.e. the sum of combined sewer system, CSS; separate sewer system, SSS; sewer and no sewer inputs) into the surface waters are relatively important for those heavy metals (Cd, Cu, Zn) widely used in building materials and traffic. Of relative growing importance is the increasing contribution of the erosion pathway for Pb, the groundwater pathway for Zn and the fast runoff pathway for Cd.

Discharge

The daily discharge was simulated for the period from 1985 to 1999. The water balance model was calibrated for the period 1985–1990 and validated for the period 1991–1999. For several gauging stations the Nash efficiency was calculated, which indicates the goodness of fit. The Nash efficiency ranged between 0·57 and 0·87 (which means a fairly good fit). In Figure 6, the simulated discharge and the measured discharge for the calibration and validation period are compared for several monitoring stations in the Elbe basin. In Table IV the results of the statistical analysis of the model calibration and validation are shown. In general, a good representation of the simulated discharge is reached, although the average simulated yearly discharge at Schnackenburg is slightly overestimated. For all rivers (except Havel) Nash efficiencies higher than 0·6 are achieved for the calibration period, which means that METALPOL represents the measured discharge fairly well. Table IV also shows the results of the statistical analysis of the model validation compared to the observed values. In general, the good representation of the simulated discharge is sustained. In some cases the Nash efficiency for the validation period is even higher than for the calibration period.

Heavy metal loads

The water quality and discharge data used in this study were gathered for several water quality stations in the Elbe drainage area. The heavy metal load within the river was calculated according to the method of OSPAR (1996), which includes a correction for the calculation of the mean yearly load. The model results are compared with measured data in Figure 7, Figure 8, Table V and Table VII. The results from METALPOL show that this model explains much of the spatial and temporal variations of the annual heavy metal loads in the River Elbe. As shown in Figure 7 and Figure 8, the spatial and temporal changes of the heavy metal

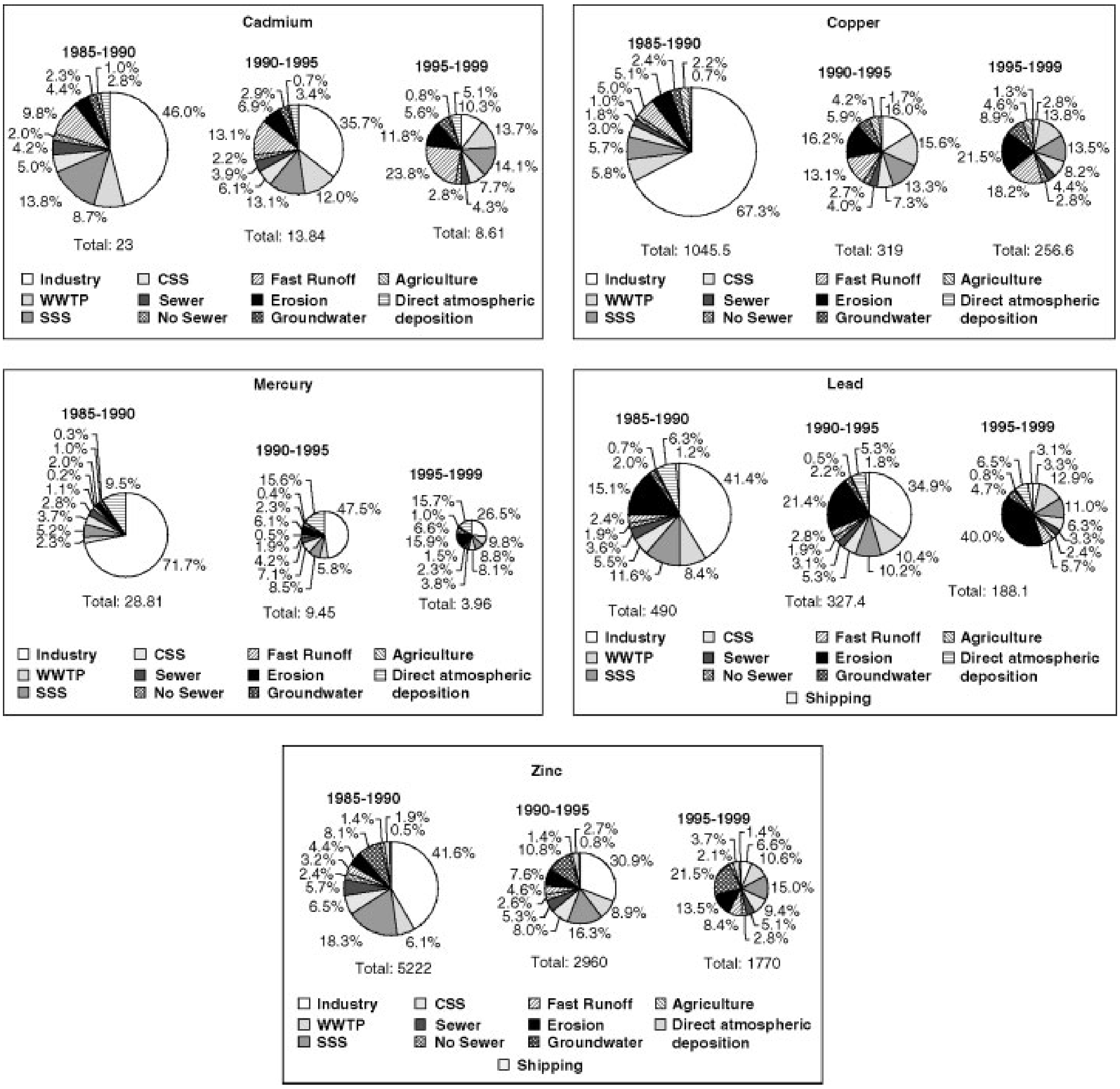


Figure 5. Heavy metal emissions into surface water (t a^{-1}) and the contribution of different point and diffuse sources and pathways in the Elbe basin over the period 1985–1999

load in the Elbe basin are successfully described. The deviations in the mid-eighties (Figure 8) are probably caused by the uncertainties in the estimated industrial and urban emissions during this period. For each heavy metal an individual retention function [as shown in Equation (2)] was estimated, since it was assumed that the natural processes influencing the losses did not change over this time period and that changes in loads are only influenced by the changes in emissions. As shown in Table V, about 81–97% of variance for the different heavy metals can be explained by the dependency on specific runoff. The estimated heavy metal retention in the Elbe basin range from 30–79% (Table VI), which is comparable to the P-losses reported by Behrendt *et al*. (1999).

Table VII shows the results of the model calibration and validation compared for the simulated heavy metal loads and measured heavy metal loads at Schnackenburg. The calibration of the heavy metal fluxes for all

Table IV. Model performance for different subcatchments for the calibration period 1985–1990 and validation period 1991–1999

Calibration period 1985–1990						
Gauging station	Observed discharge (m^3 s^{-1})	Simulated discharge (m^3 s^{-1})	Standard deviation observed	Standard deviation simulated	Nash efficiency	$Error_{cal}$
Schönau	293·1	339·9	98·8	122·0	0·60	46·7
Decin	321·8	339·0	108·8	121·4	0·89	23·8
Dessau	61·2	72·1	25·4	26·4	0·76	10·9
Ammendorf	16·2	14·7	6·8	4·3	0·71	2·3
Calbe-Grizehne	122·8	110·4	42·9	33·3	0·80	12·4
Magdeburg	552·1	504·2	191·3	181·6	0·87	55·6
Cottbus	20·1	19·6	4·9	5·5	0·83	2·1
Havelberg	105·8	93·5	29·6	34·5	0·57	16·7
Neu Darchau	654	691	228	245	0·91	37·2

Validation period 1991–1999						
Gauging station	Observed discharge (m^3 s^{-1})	Simulated discharge (m^3 s^{-1})	Standard deviation observed	Standard deviation simulated	Nash efficiency	$Error_{val}$
Schönau	330·5	280·3	78·5	71·3	0·45	48·2
Decin	329·7	285·3	78·2	81·3	0·55	28·3
Dessau	64·8	59·3	25·2	19·2	0·40	12·2
Ammendorf	23·6	24·9	9·2	10·3	0·77	2·4
Calbe-Grizehne	104·7	110·2	38·7	30·9	0·77	10·8
Magdeburg	471·3	507·2	143·1	132·9	0·52	79·5
Cottbus	18·9	13·8	4·1	2·8	−1·54	5·7
Havelberg	94·1	94·2	31·1	26·8	0·84	11·0
Neu Darchau	657·1	617·9	193·1	159·2	0·64	82·0

Table V. Results of regressions between heavy metal retention and the specific runoff for the Elbe basin

Parameters	Cadmium	Copper	Mercury	Lead	Zinc
r^2	0·90	0·81	0·94	0·89	0·97
a	5·8	9·3	7·9	12·0	6·9
b	−1·0	−1·3	−1·3	−0·8	−1·3

individual stations was difficult for the time period 1985–1990. This is caused by the lack of measured heavy metal load data for several monitoring stations over this time period. In general, the good representation of the simulated heavy metal loads is maintained or improved in the validation period 1991–1999. In some cases the model efficiency for the validation period is even higher than for the calibration period. This confirms again that the model performance is relatively good.

MODEL UNCERTAINTY AND SENSITIVITY

The main scientific uncertainties are caused by uncertainties in the magnitude of the sources and sinks of heavy metals in large river basins (Foster and Charlesworth, 1996). Generally, the heavy metal emissions

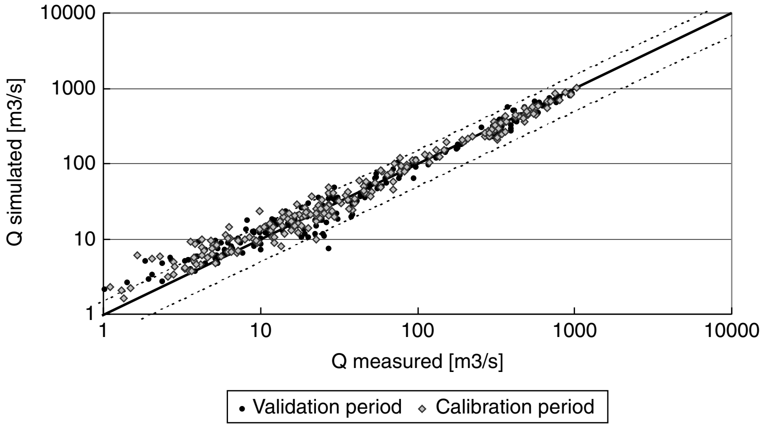


Figure 6. Simulated versus measured discharge for several monitoring stations for the calibration (1985–1990) and validation period (1995–1999)

Table VI. Average percentage of the heavy metal emissions temporarily or permanently retained in the river system over the time period 1985–1999

	Elbe	Mulde	Saale	Havel	Czech Republic
Cd	51	37	55	59	53
Cu	51	35	56	60	45
Hg	48	32	54	57	42
Pb	75	66	78	79	73
Zn	45	30	50	54	39
P (according to Behrendt and Opitz, 1999)	61	38	62	66	55

Table VII. Model performance for Schnackenburg (total Elbe basin) for the calibration period 1985–1990 and validation period 1991–1999

Calibration period 1985–1990					
	Cd	Cu	Hg	Pb	Zn
$L^M_{\text{obs},i,t}$[t a^{-1}]	10·7	379	18·3	116	2507
$L^M_{\text{sim},i,t}$[t a^{-1}]	11·5	495	14·4	120	2775
ME	0·8	0·6	0·6	0·9	0·8
L_Error$_{\text{cal}}$	1·6	87	4·2	11·1	273
Validation period 1991–1999					
	Cd	Cu	Hg	Pb	Zn
$L^M_{\text{obs},i,t}$ [t a^{-1}]	5·6	118	3·1	78·6	1232
$L^M_{\text{sim},i,t}$ [t a^{-1}]	4·8	134	2·9	56·7	1168
ME	0·52	0·86	0·96	−1·0	0·91
L_Error$_{\text{val}}$	0·8	39	2·3	7·8	363

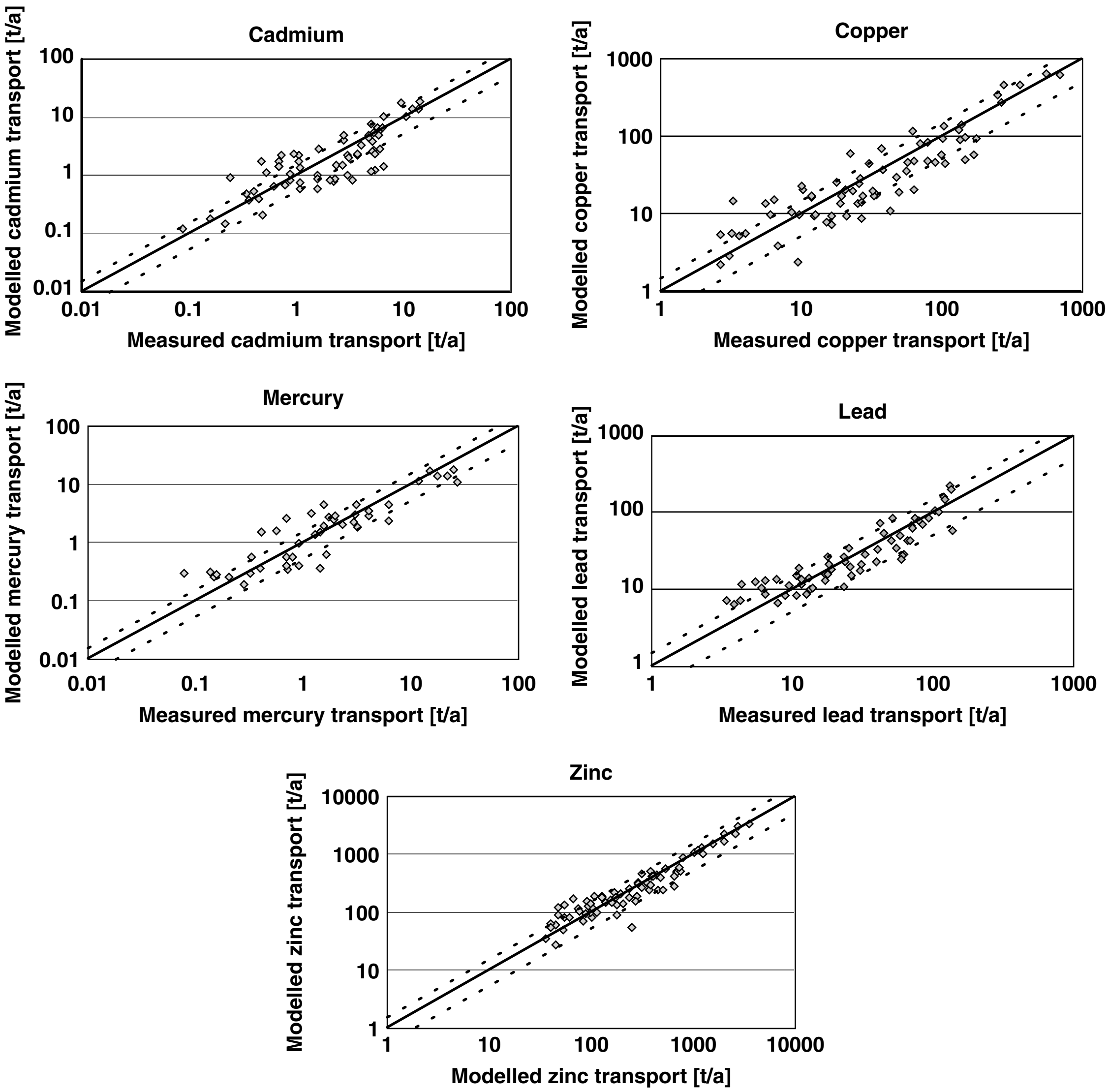


Figure 7. Simulated and measured heavy metal loads for several monitoring stations

are estimated with statistical characteristics of the region or subregions and emission factors derived from several emission studies (Stigliani and Anderberg, 1992; Stigliani and Jaffe, 1992). The problem with these emission factors is that they are site-specific in that they are developed for a certain region or country (Foster and Charlesworth, 1996). Further, uncertainties in emission factors are not well known. Most uncertainties in the heavy metal emissions are caused by a lack of adequate coverage and inaccuracies in representative data on heavy metal emissions. A further source of uncertainties is the knowledge of key physical and chemical processes on the scale of a river basin, which has a bearing on the transport of heavy metals through the soil to the groundwater and river network. It is not uncommon for more than 90% of the total heavy metal load in rivers to be transported in the solid phase, either sorbed onto particle surfaces and coatings, or incorporated into mineral grains. Fluvial geomorphic processes are therefore of fundamental importance in the transport and fate of heavy metals (Foster and Charlesworth, 1996). Other uncertainties are the role of processes of retention

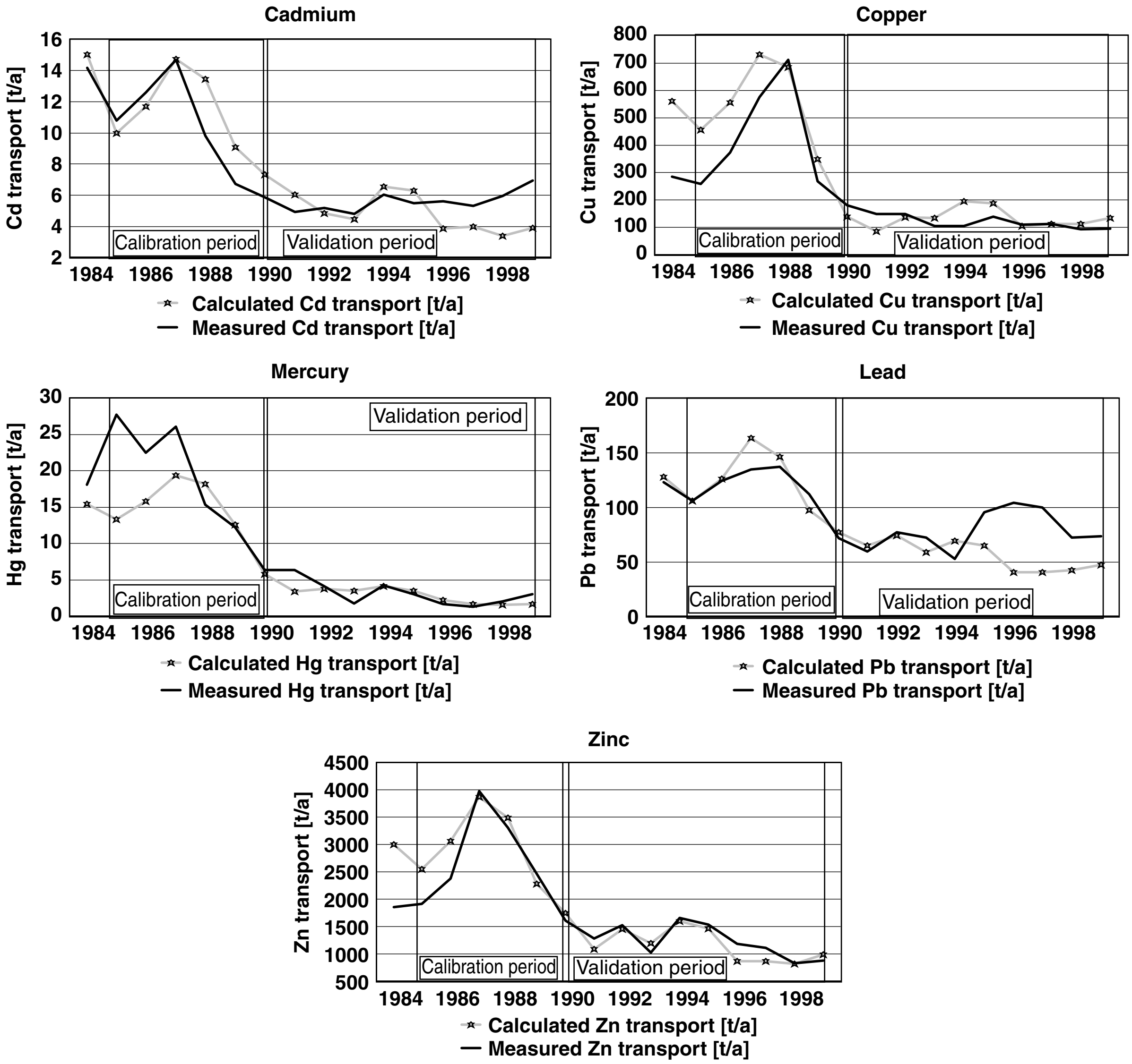


Figure 8. Simulated and measured average load at the catchment outlet Schnackenburg. Temporal variation

(sedimentation) and release (resuspension) of material within the river network (Foster and Charlesworth, 1996). A discrepancy between measured heavy metal loads and heavy metal inputs into a river system exists (Behrendt, 1993; Vink *et al*., 1997, 1999b). Asselman (1997) reported a net loss of sediments, due to overbank sedimentation. During an extreme flood event in 1993, 8% of the average annual sediment load transported by the River Rhine into The Netherlands had been deposited on its floodplain. A loss of heavy metals in reservoirs and lakes through sedimentation of suspended solids has been reported by various authors (Arnold *et al*., 1997, Müller *et al*., 1998). An approach to investigate the influence of uncertainties in calibrated model parameters on the model outcome is to do a sensitivity analysis. A sensitivity analysis studies the influence of variations in the uncertainty sources and model parameters on the model outputs. The uncertainty sources and model parameters are varied over a range of possible values.

Water balance

A robust model will not be sensitive to (small) changes of model parameters, which is helpful if the parameters cannot be calibrated independently with observed values. The sensitivity of the simulated discharge (by the model METALPOL) to the land use factor, maximum water holding capacity of the soil, rainfall, hydrogeology and fast runoff coefficients was investigated in order to determine which of these parameters exert a greater control over the model output. The analysis consisted of an error analysis of the model given a certain error in input. This is commonly done by imposing a change in input variables; in this case land use factor, maximum water holding capacity of the soil, rainfall, hydrogeology and fast runoff coefficients. The results of these analyses are presented in Figure 9, expressed as the average simulated discharge for each relative change in the considered parameter. Figure 9 shows that the model results are very sensitive to changes in the amount of rainfall and the land use factor and less sensitive for changes in hydrogeology and fast runoff coefficients.

Heavy metal loads

The sensitivity of the simulated heavy metal loads (by the model METALPOL) to the rainfall, erosion, direct emissions and land use was investigated in order to determine which of these parameters exert a greater control over the modelled output. Again, the analysis consisted of an error analysis of the model given a certain error in input. This was done by imposing a change in input variables. The results of these analyses are presented in Figure 10, expressed as the model heavy metal load for each relatively changed parameter. Figure 10 shows that the heavy metal loads are very sensitive to changes in the amount of rainfall and emissions from point and direct (urban) sources. The simulated heavy metal loads are least sensitive to changes in heavy metal emissions from agricultural diffuse sources. Of course, these heavy metal emissions directly influence the heavy metal concentrations of the top soil.

COMPARISON OF METALPOL TO OTHER HEAVY METAL EMISSION STUDIES

In the next section a comparison is made between the results from METALPOL and other studies. The contribution of the different point and diffuse emissions into the surface waters estimated with METALPOL is compared to the results from Böhm *et al*. (2000) and Vink and Behrendt (2002). The estimated point and

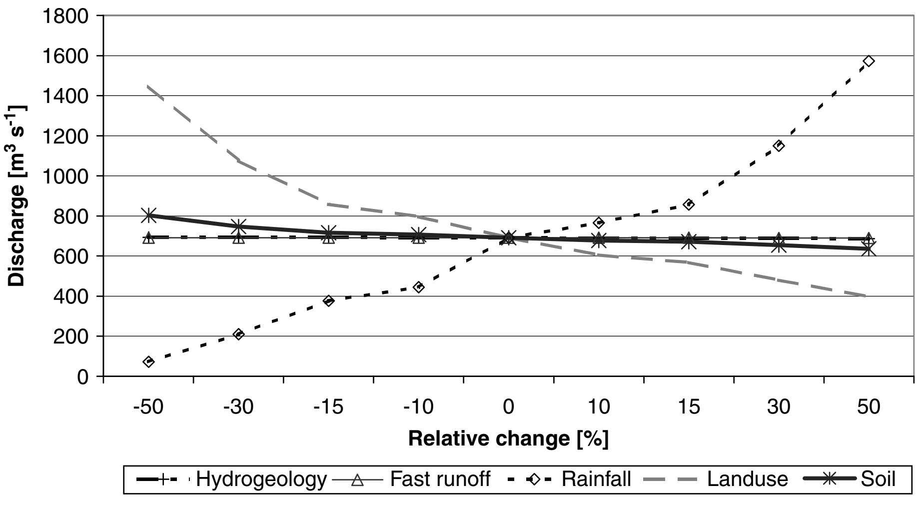


Figure 9. Model sensitivity to rainfall, maximum water holding capacity, land use factor, hydrogeology and fast runoff coefficients

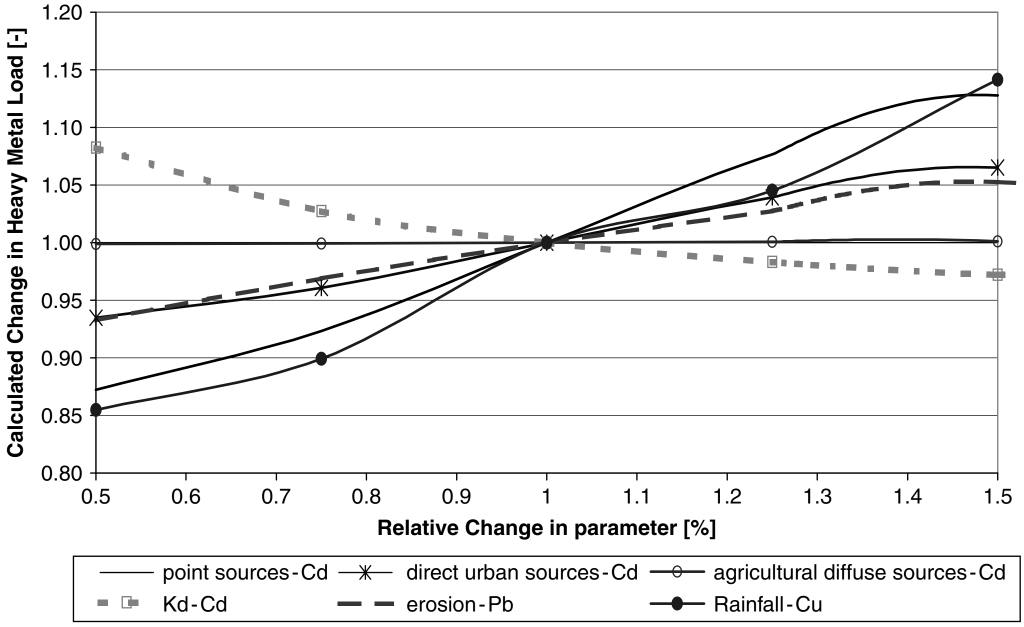


Figure 10. Model sensitivity to changes in rainfall (Cu), erosion (Pb), point and diffuse heavy metal emissions and Kd (Cd)

diffuse emissions from Böhm *et al.* (2000) and Vink and Behrendt (2002) were calculated with the MONERIS model for the Elbe basin over the period 1993–1997; as shown in Table VIII. The difference between the results from Böhm *et al.* (2000) and the other studies in the industrial heavy metal emissions in the Elbe basin is caused by the fact that Böhm *et al.* (2000) only included the industrial heavy metal emissions from the German part of the Elbe basin in the year 1998 and did not include the industrial emissions from the Czech Republic.

Generally, the total heavy metal emissions estimated by Böhm *et al.* (2000) are lower than the heavy metal emissions estimated with METALPOL by Vink and Behrendt (2002), except for copper. Further, the contribution of the point and diffuse sources (%) reported by Böhm *et al.* (2000) is in general higher than that estimated with METALPOL by Vink and Behrendt (2002). One of the pathways which shows large differences is the heavy metal emissions from urban areas. This is caused by the lower urban deposition in the studies of Böhm *et al.* (2000). The contribution of wastewater treatment plants is also lower in the Böhm *et al.* (2000) model, which is caused by the different method for calculating these heavy metal emissions from wastewater treatment plants. The comparison of Vink and Behrendt (2002) and METALPOL shows that although the total heavy metal emissions are relatively similar, the contribution of the different individual pathways shows some large differences. This difference in heavy emissions is observed in the fast runoff pathway. In METALPOL this pathway is modelled with Kd-concept and in MONERIS through estimated/measured concentrations in drainage and surface runoff. This problem of estimating indirect diffuse heavy metal emissions, such as groundwater, surface runoff and erosion, along the individual pathways cannot be solved since there is no method available to measure these individual heavy metal fluxes.

SCENARIO ANALYSIS

Although in the period 1985–1999 a considerable reduction in emissions and an improvement of water quality has been achieved, the amount of heavy metals in water, suspended matter and sediments is in some cases still too high to achieve the targets set by the German government. This means that a further reduction in

Table VIII. Comparison of METALPOL to Vink and Behrendt (2002) and Böhm *et al.* (2000)

Source	Cd [t a^{-1}]			Cu [t a^{-1}]			Hg [t a^{-1}]			Pb [t a^{-1}]			Zn [t a^{-1}]		
	MET[a]	Vink[b]	Böhm[c]	MET[a]	Vink[b]	Böhm[c]	MET[a]	Vink[b]	Böhm[c]	MET[a]	Vink[b]	Böhm[c]	MET[a]	Vink[b]	Böhm[c]
Industry	1·5	1·5	0·53	14·5	14·5	7·5	1·96	1·96	0·06	17	16·8	9·2	217	217	23·8
Wastewater treatment plant	1·3	1·8	0·7	39·7	50·2	18·1	0·44	0·46	0·2	27·1	33·5	7·4	209·4	268	107·2
Atmospheric deposition	0·45	0·4	0·43	3·9	7·7	6·5	0·8	0·05	0·04	14	8·8	8·7	71·9	55	54·2
Surface runoff		0·1	0·01		5·5	2·0		0·02	0·01		1·1	1·2		18	12·1
Drainage	2·2	0·4	0·8	51·8	14·0	13·9	0·06	0·09	0·1	11·7	4·4	3·8	168	56	156·2
Erosion	1·1	0·9	0·5	56·7	60·0	73·8	0·65	0·38	0·26	77·3	67·4	48·0	247	187	179·4
Groundwater	0·5	0·8	0·3	24·2	39·3	153	0·28	0·19	0·15	9·3	10·9	12·7	409·1	290	53·6
Urban areas	2·8	3·2	1·44	78·0	72·1	67·6	1·23	1·66	0·44	49·9	54·7	36·7	683·3	885	406
Other diffuse sources	0·07	0	0	11·9	0	4·2	0·04	0	0·0	7·5	0	1·0	62	0	6·53
Total emissions	9·9	9·2	4·7	281	264	347	5·5	4·8	1·3	214	198	128	2067	1976	999
Point sources (%)	28	36	26	19	25	7	45	50	21	21	25	13	21	25	13
Diffuse sources (%)	72	64	74	81	75	93	55	50	79	79	74	87	79	75	87

[a] MET gives the METALPOL results as presented.
[b] Vink gives the results from Vink and Behrendt (2002).
[c] Böhm illustrates the results from Böhm *et al.* (2000).

future emissions is desirable, as already described in the action programme of the International Commission for Protection of the River Elbe (IKSE, 1998). The objective of this paper is to indicate which reductions in the emissions to the surface waters would be feasible at various levels of environmental efforts. The analysis has been made using four scenarios. The four scenarios presented here are primarily intended as framework scenarios for specialized studies focusing on different effects; the scenarios also provide a link to the policy areas of land use planning, climate change and urban development. The scenarios are exploratory and follow different trends based on diverging assumptions about policy development in Europe and in the individual countries. In Table IX the measures and developments in the different scenarios are briefly summarized.

The '*Business As Usual*' (BAU) scenario is restricted to the current situation and only includes those measures likely to be implemented within the next five years.

Table IX. Measures and developments in the different scenarios

Source/sector	BAU	Green environment	Climate change	Land use change
Industry	No reduction measures (same level as 1999)	BAT measures give 15% reduction	No reduction measures (same level as 1999)	No reduction measures (same level as 1999)
WWTP	All WWTPs of category 3 include a denitrification step and all WWTPs of category 4 have implemented a P-elimination step	Includes all measures in BAU, a P-elimination step in all WWTPs of category 3 and microfiltration techniques in the largest WWTPs (category 5)	All WWTPs of category 3 include a denitrification step and all WWTPs of category 4 have implemented a P-elimination step	All WWTPs of category 3 include a denitrification step and all WWTPs of category 4 have implemented a P-elimination step
Direct atmospheric deposition	No reduction measures	No reduction measures	No reduction measures	No reduction measures
Urban areas	No reduction measures	Active replacement of building materials (e.g. coating of lead sheet and galvanized steel). Use of longer lasting car tyres and infiltration of runoff from roads. Decoupling of paved urban areas from the sewer system. Enlargement of rainwater storage basins in urban areas	No reduction measures	Growth of urban areas and forests
Erosion	No reduction measures	Extra measures to reduce erosion in steep areas	No reduction measures	No reduction measures
Groundwater	No reduction measures	No reduction measures	No reduction measures	No reduction measures
Drainage	No reduction measures	No reduction measures	No reduction measures	No reduction measures
Surface runoff	No reduction measures	No reduction measures	No reduction measures	No reduction measures
Agriculture	No reduction measures	Reduction of fertilizer use and livestock	No reduction measures	Reduction of fertilizer use and livestock
Soil	No change	No change	No change	Decline of pH by 0·5 units
Climate	No change	No change	Increase in rainfall and temperature	No change

The '*Green Environment*' (GE) scenario assumes additional measures taken to prevent emissions at the source (e.g. industry) and measures taken in the infrastructure (e.g. level of sewer connections, upgrading of wastewater treatment). The GE scenario aims to reach water quality standards and emission reduction goals as soon as possible and to a maximum extent.

The '*Land Use Change*' (LUC) scenario focuses on future land use and is linked to agricultural and land use planning policy areas. The LUC scenario does not foresee radical changes in the food sector in Europe. The scenario is based on past development of land use in the Elbe basin.

The '*Climate Change*' (CC) scenario focuses on future changes in rainfall and temperature and includes measures from the BAU scenario.

In Figure 11 an overview is g/iven of the estimated heavy metal emissions in the Elbe basin for the four scenarios in comparison to the heavy metal emissions in 1999. The results from the BAU scenario show that heavy metal emissions from wastewater treatment plants are reduced by 37% in 2020 in comparison to the situation in 1999. This is caused by the implementation of the European Union (EU) urban wastewater treatment directive in National German law and National Czech law (assuming that the Czech Republic joins the EU), which demands upgrading of wastewater treatment plants. This decrease in heavy metal emissions from wastewater treatment plants is counteracted by an increase in heavy metal emissions from urban areas caused by the growing amount of population, houses and traffic in urban areas and thus the total heavy metal emissions in the Elbe basin generally only decrease slightly or even increase in the case of Cu.

The GE scenario shows that measures in urban areas (decoupling of paved urban area, increase of retention capacity and decrease of urban deposition rates) cause a 50–63% reduction in the heavy metal emissions from urban areas. The extra microfiltration step in larger wastewater treatment plants also has a positive effect on the emissions from wastewater treatment plants and decreases heavy metal emission by 64%. The total heavy metal emissions decline by about 30% when compared to the 1999 situation.

The CC scenario shows that measures in urban areas (decoupling of paved urban area, increase of retention capacity and decrease of urban deposition rates) cause a 50–63% reduction in the heavy metal emissions from urban areas.

The LUC scenario assumes declining state support for the agricultural sector and only small increases in future demands for food products (Prieler *et al*., 1998). Reforestation of marginal farmland occurs, because of the growing demand for timber products as well as other recreational uses of forest areas. This abandonment of agricultural land will cause a decline in the pH of the soils (Romkens, 1998). The extent of the pH decline will depend on the soil characteristics, former agricultural practices and acid deposition. The pH decline was assumed to be 0·5 until 2020. The influence of a decline in pH mostly affects cadmium and zinc emissions by fast runoff and causes total heavy metal emissions to increase by about 40%. A sustainable situation, which ends discharges of hazardous (noxious, persistent and bioaccumulating) substances by the year 2020 (ICPNS, 1995), based on the assumptions in the scenario analyses, is not expected to be achieved until 2020. This indicates the need for further efforts in the Elbe basin, beyond reduction measures already accounted for in the BAU and GE scenarios.

CONCLUSIONS

Considering the uncertainties in the measured heavy metal loads, heavy metal emissions and representation of the modelled processes, METALPOL predicts the heavy metal fluxes throughout the Elbe basin well enough for the purposes of this study. The results are constrained by the ability to derive model parameters from digital data sets. It seems possible to explain part of the spatial and temporal variations in heavy metal load without a detailed description of all processes occurring on the small scale. The results from METALPOL illustrate that the developed calculation method is applicable for the estimation of heavy metal fluxes in large river basins such as the Elbe basin. The results of this study can additionally support the implementation of the EU Water Framework Directive. The regional differences in various subcatchments (e.g. differences in

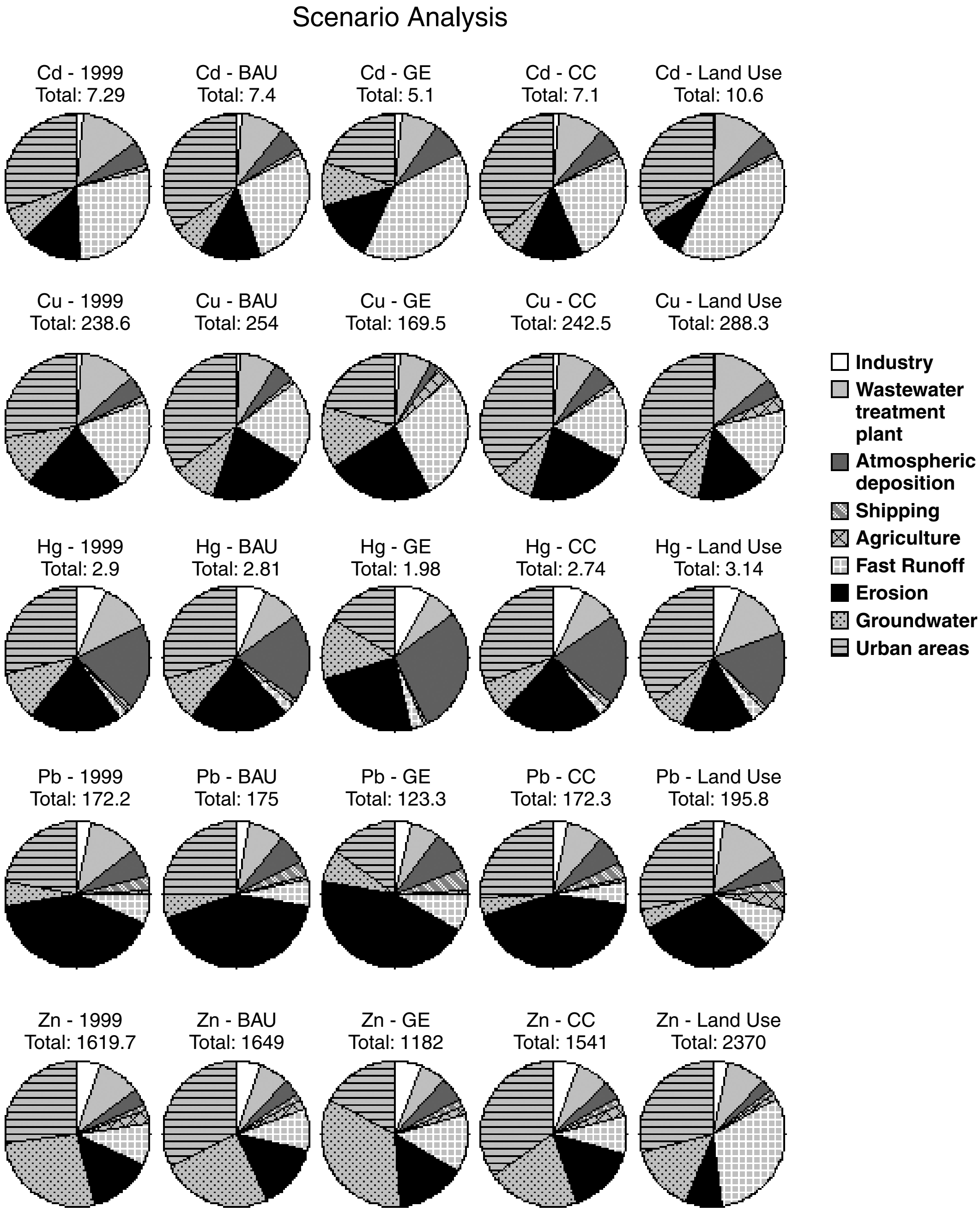


Figure 11. Predicted effects of the emission reduction measures in the scenario analysis. Fluxes of heavy metals for 2020 (t a^{-1})

connectivity to wastewater treatment plants, erosion, drainage and volumes of retention basins, etc.) can be visualized. The validation results demonstrate that the regional differences in heavy metal loads, the temporal trends and changes in heavy metal loads are in reasonable agreement with the measured heavy metal loads. Heavy metal emissions from wastewater treatment plants rather than emissions from industries nowadays dominate the point source emissions. Both the absolute and relative amount of heavy metal emissions caused by point sources (the sum of industries and wastewater treatment plants) in the Elbe basin have rapidly decreased. The contribution of point sources to the total emissions over the period 1995–1999 ranges from 16% (Pb) to 36% (Hg). Whereas the absolute contribution of diffuse sources is also decreasing, the relative contribution of diffuse sources to the total heavy metal emissions is increasing in the Elbe basin. The relative contribution of diffuse source emissions to the total heavy metal emissions ranges from 64% (Hg) to 84% (Pb). Further, direct heavy metal emissions from urban areas (i.e. the sum of CSS, SSS, sewer and no sewer) into the surface waters are relatively important for those heavy metals (Cd, Cu, Zn) widely used in building materials and traffic. The sensitivity and uncertainty analysis presented in this paper also illustrates that the reliability of the model simulations is directly affected by the quality of the input data (especially point source and urban emissions) and the distribution of the input data like rainfall data, emission data, soil data and land cover data. Of course, the resolution of the model (1 km^2) strongly simplifies the catchment characteristics and input data. The loss of spatial and temporal resolution associated with the use of large-scale data causes this model to be unsuitable for small-scale analysis (basins smaller than 1000 km^2) and simulation of loads over short time periods. Prediction of the total heavy metal emissions is possible when the heavy metal load and the main characteristics of the basin such as basin size and specific runoff for a certain time period are known. The derived conceptual model for heavy metals allows the description of the retention behaviour of each of the various heavy metals in large river basins. The calculated heavy metal retention in the Elbe basin is in good agreement with the values reported by Behrendt and Opitz (1999) and ranges from 30% for Zn to 79% for Pb. One of the shortcomings of METALPOL is the lack of a description of the interaction of the river with the floodplains (resuspension and erosion events). Scenario analysis indicates the need for further efforts in the Elbe basin, beyond reduction measures already accounted for in the BAU scenario. Future policy options should focus more on the reduction of emissions from diffuse sources, since the emission analysis shows that the contribution of these diffuse sources is more than 70% of the total heavy metal emissions.

REFERENCES

Arnold A, Hanisch C, Hänsel C, Jendryschik K, Müller A, Zerling L. 1997. Bestandsaufnahme der Schwermetall situation im Gewässersystem der Weiβen Elster und im Bitterfelder Muldestausee. In *Die Belastung der Elbe*, Teil I, Elbenebenflüsse. Forschungszentrum Karlsruhe GmbH: Karlsruhe.

Asselman N. 1997. *Suspended sediment in the river Rhine: the impact of climate change on erosion, transport and deposition*. PhD thesis, no. 234, University of Utrecht, Netherlands.

Behrendt H. 1993. *Point and diffuse loads of selected pollutants in the River Rhine and its main tributaries*. RR-93-1, IIASA, Laxenburg, Austria.

Behrendt H, Opitz D. 1999. Retention of nutrients in river systems: dependence on specific runoff and hydraulic load. *Hydrobiologia* **410**: 111–122.

Behrendt H, Huber P, Kornmilch M, Opitz D, Schmoll O, Scholz G, Uebe R. 1999. *Nährstoffbilanzierung der Flussgebiete Deutschlands*. UBA-Texte 75/99, Berlin, Germany.

Böhm E, Hillenbrand T, Marscheider-Weidemann F, Schempp C, Fuchs S, Scherer U, Lüttgert M. 2000. *Emissionsinventar Wasser für die Bundesrepublik Deutschland*. UBA-Texte 53/00, Berlin, Germany.

de Wit MJM. 1999. *Nitrogen fluxes in the Rhine and Elbe basins*. PhD thesis, University of Utrecht.

Fauth H, Hindel R, Siewers U, Zinner I. 1985. *Geochemischer Atlas Bundesrepublik Deutschland*. Bundesanstalt für Geowissenschaften und Rohstoffe, Schweizerbart'sche Verlagsbuchhandlung: Stuttgart.

Foster IDL, Charlesworth M. 1996. Heavy metals in the hydrological cycle: trends and explanation. *Hydrological Processes* **10**: 227–261.

IAH. Various years. *International Hydrogeological Map of Europe* (various sheets). UNESCO: Paris.

ICPNS. 1995. Esbjerg declaration—Ministerial Declaration of the Fourth International Conference on the Protection of the North Sea.

IKSE. 1992. Inventar wichtiger Abwassereinleiter im Einzugsgebiet der Elbe im Jahre 1989. Magdeburg, Germany.

IKSE. 1995. Bestandsaufnahme von bedeutenden punktuellen kommunalen und industriellen Einleitungen von prioritären Stoffen im Einzugsgebiet der Elbe.

IKSE. 1998. Erster Bericht über die Erfüllung des 'Aktionsprogramms Elbe'. Magdeburg, Germany.

IKSE. 2000. Zweiter Bericht über die Erfüllung des 'Aktionsprogramms Elbe' im Zeitraum 1998 und 1999. Magdeburg, Germany.

IKSR (Internationale Kommission zum Schutze des Rheins). 1999. *Bestandsaufnahme der Einträge prioritärer Stoffe 1996*. IKSR-Dokument, Koblenz.

Kwadijk J. 1993. *The impact of climate change on the discharge of the river Rhine*. PhD thesis, University of Utrecht.

LABO. 1998. Hintergrundwerte für anorganische und organische Stoffe in Böden. In *Handbuch des Bodenschutzes*, Rosenkranz D (ed.). Erich Schmidt Verlag: Berlin.

Mohaupt V, Sieber U, Van De Roovaart J, Verstappen CG, Langenfeld F, Braun M. 2000.. Diffuse sources of heavy metals in the rhine basin. In *4th Conference on Diffuse Pollution*, International IAWQ Proceedings, Bangkok.

Müller A, Hanisch H, Zerling L, Lohse M, Walther A. 1998. *Schwermetalle im Gewässersystem der Weißen Elster. Natürliche und anthropogene Elementverteilung im Sediment, im Schwebstoff, und in der gelösten Phase*. Abhandlungen der Sächsischen Akademie der Wissenschaften zu Leipzig, Band 58, Heft 6.

OSPAR (Oslo–Paris Commission). 1996. Principles of the comprehensive study of riverine inputs and direct discharges (RID).

PC-Raster. 1996. *Environmental Software—Manual version 2*. Department of Physical Geography, University of Amsterdam: Amsterdam.

Prieler S, Lesko A, Anderberg S. 1998. *Three scenarios for land-use change: a case study in Central Europe*. WP-98-3, IIASA, Laxenburg, Austria.

Rogler H, Schwertmann U. 1981. Erosivität der Niederschläge und Isoerodentkarte von Bayern. In *Zeitschrift für Kulturtechnik und Flurbereinigung* **22**.

Romkens P. 1998. *Effect of land use changes on organic matter dynamics and trace metal solubility in soils*. PhD thesis, University of Groningen: Groningen.

Stigliani WM. 1988. Changes in valued 'capacities' of soils and sediments as indicators of nonlinear and time-delayed environmental effects. *Environmental Monitoring and Assessment* **10**: 245–307.

Stigliani WM, Anderberg S. 1992. *Industrial metabolism in the Rhine basin*. RR-92-10, IIASA, Laxenburg, Austria.

Stigliani WM, Jaffe PR. 1992. *Industrial Metabolism: a new approach for analysis of chemical pollution and its potential applications*. RR-92-06, IIASA, Laxenburg, Austria.

Vink RJ. 2002. *Heavy metal fluxes in the Elbe and Rhine river basins: analysis and modelling*. PhD thesis, University of Amsterdam: Amsterdam.

Vink RJ, Behrendt H. 2002. Emissions, immissions and retention processes of heavy metals in the Rhine and Elbe drainage areas and their tributaries. *Hydrological Processes* **16**: 3227–3244.

Vink RJ, Behrendt H, Salomons W. 1997. *Point and diffuse source analysis of heavy metals in the Elbe drainage area: comparing heavy metal emissions with transported river loads*. GKSS-report, Germany.

Vink RJ, Behrendt H, Salomons W. 1999a. Development of the heavy metal pollution trends in several European rivers: an analysis of point and diffuse sources. *Water, Science and Technology* **39**(12): 215–223.

Vink RJ, Behrendt H, Salomons W. 1999b. Point and diffuse source analysis of heavy metals in the Elbe drainage area: comparing heavy metal emissions with transported river loads. *Hydrobiologia* **410**: 307–314.

